NWC TP 5944

# Cinephotomicrography and Scanning Electron Microscopy as Used To Study Solid Propellant Combustion at the Naval Weapons Center

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Naval Weapons Center
CHINA LAKE, CALIFORNIA 93555

# Naval Weapons Center

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R. G. Freeman, III, RAdm., USN ..... Commander

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## FOREWORD

Members of the Aerothermochemistry Division, Research Department, Naval Weapons Center, were among investigators pioneering the use of cinephotomicrography and scanning electron microscopy in studying solid propellant combustion. This work was started in the early 1960s and has been used in many programs since that time. Sponsors of this work have included: National Aeronautics and Space Administration under Work Orders 11, 294, 3034, 3035, and 6030; the Naval Air Systems Command under AIRTASK A310310C/008A/3R02402002; and the Naval Sea Systems Command under ORDTASK 331-001/200-1/URO-100-202, ORD-033129/200, 1/R001-06-01PA5, and SEATASK 331-001/200-1/URO 24-02-02.

Discussion of the performance of commercially available equipment or products in this report does not constitute an endorsement of any piece of equipment or product.

This report has been reviewed for technical accuracy by R. L. Derr.

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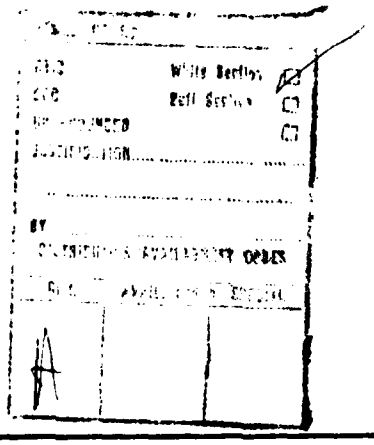
(U) This report discusses cinephotomicrography and scanning electron microscopy, and how these techniques have been used by investigators studying solid propellant combustion. The elements required for taking and using high speed, high magnification motion pictures – cameras, lenses, window bombs, light sources, timers, hot-stage microscopes, motion analyzers – are discussed. The principles and equipment needed for scanning electron microscopy are also discussed.



CONTENTS

## INTRODUCTION

Combustion of solid propellants is a dynamic process with events occurring rapidly and within short distances. For example, a single ammonium perchlorate (AP) crystal undergoing self-deflagration regresses at a rate of approximately 0.5-1.5 cm/s. In less than a second an element of AP can undergo the following (illustrated in Figure 1):

1. Phase change from orthorhombic AP to cubic AP
2. Formation of a liquid surface
3. Formation and liberation of gases through the liquid with subsequent microreactions
4. Vaporization of products
5. Some further reaction of products

All the above processes occur in a layer less than 100 μm thick and in less than 1 second; that is for the simple case of combustion of a relatively large homogeneous solid. It is much more difficult to study the combustion of aluminized solid propellants with a built-in heterogeneity--the ingredient particles sizes are on the same scale as the reaction zones.

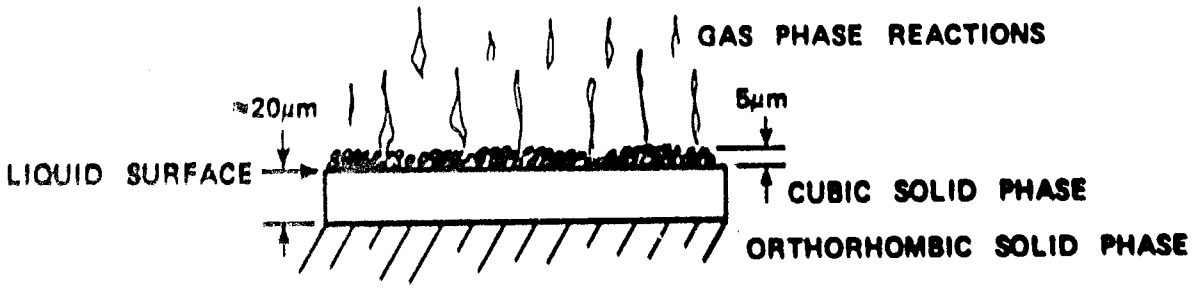



FIGURE 1. Typical Dimension.

Obviously, if processes as spatially and temporally complex as the combustion of solid propellants are to be studied, tools are needed which can magnify the spatial details and slow the viewing of the reactions (without changing the reaction being studied). This paper describes two such tools which have been used extensively at the Naval Weapons Center (NWC): cinephotomicrography (high speed, high magnification movies) and scanning electron microscopy (SEM). Cinephotomicrography magnifies the spatial details (film images up to several times larger than the actual object) and also stretches out time by orders of magnitude (pictures taken at several thousand frames/s and projected at tens of frames/s). SEM enables one to look at the surface of samples, such as propellants which were quenched during combustion, at up to several thousand times magnification.

It is the purpose of this paper to briefly describe these two tools and illustrate their usefulness in studying solid propellant combustion by providing examples from work done at NWC. The purpose is not to provide in-depth descriptions of the tools (references to more detailed descriptions of cinephotomicrography and SEM are provided for the person desiring more information), nor detailed explanations for all reactions taking place during combustion of propellants and/or their ingredients (a bibliography is provided for those desiring detailed information).

## CINEPHOTOMICROGRAPHY

### BACKGROUND

Cinephotomicrography is a good method for studying surface detail and surface regression occurring during combustion, as well as observing the structure of luminous flames. It is an ideal technique for several reasons:

1. It is a primary observation--no data reduction is required for qualitative understanding and the simplest data reduction is all that is required for quantitative measurement of size and burning rates.

2. It provides a visual record--the old cliches "A picture is worth a thousand words" and "seeing is believing" seem appropriate.

3. It is a sequential recording--by playing back a sequential series of pictures, relative motion can be observed.

4. It is a "time microscope"--because the combustion behavior is filmed at several hundred to several thousand frames/s, and then projected at 1 to 24 frames/s, a "time magnification" is achieved. For example, if the camera had a framing rate of 4000 pictures per second (pps) and the resulting film was projected at 16 pps, a 250:1 time magnification would have resulted.

5. It is like an optical microscope--magnification (ratio of image size on the film to size of actual object) of several times is possible. Further magnification occurs when the film is projected via the optics of the projector. Resolution to several microns can be achieved.

Several components are required for combustion studies. One must be concerned with movie camera optics, window bombs, light sources, projectors, timing devices, motion analyzers, hot stages for microscope, and such things as infrared filters. It is the purpose of the next part of the paper to discuss each of these components.

## CAMERAS

The camera is the heart of any cinephotographic technique. Several types of cameras are commercially available. These cameras range from pin-types, having framing rates from tens to several hundred frames/s, to rotating mirror cameras having framing rates of several hundred to hundred thousand frames/s. Table 1 gives a brief outline of the camera types, speeds, and capacities.

In the combustion of solid propellants one is normally interested in regression rates of from 0.1 to 5.0 cm/s, samples approximately 1-2 cm in length, and framing rates from 400-4000 pps. Although many types of cameras are available for these studies, this report will discuss only the pin and rotating prism cameras since they are the most widely used.

TABLE 1. Types of Cameras Used for Cinephotography.

| Camera type | Framing rate | Capacity |
|---|---|---|
| Pin-type | 4-500 pps | Up to 400 feet 16 mm film reels<br>Up to 1200 feet 16 mm film reels externally mounted |
| Rotating prism | 10-44,000[a] pps | Up to 2000 feet 16 mm film reels |
| Rotating mirror | Up to $5 \times 10^6$ pps | ≈25 frames |

[a]Quarter-frame format.

## Pin-Type Framing Cameras

The pin-type camera is one of the simplest cameras to understand because it is an intermittent framing camera. That is, a frame of motion picture film is positioned in line with a window, a shutter opens exposing that frame, the shutter closes, and the film is transported so that the next frame is in the window. This process is simply repeated frame after frame. The heart of this type camera is the film transport and register assembly. Various types of transport and register techniques are used by different manufacturers but essentially they are the same. A frame is registered by the register pins engaging the sprocket holes at the film's edge. Upon exposure of the frame, the register pins draw clear for 1/2 of a framing cycle and a pull down claw, or shuttle, moves the film forward. As the pull-down claws disengage, the film is at its approximate registration point and the register pins seek the center of the upper film sprocket holes. The register pins are designed to ensure positive registering action and hold the film steady while the pull-down claws are sequencing through the back cycle and are repositioning for the next pull-down cycle. This type of design ensures that at no time during exposure is the film free to move out of the control position - positioning that makes pin-type cameras so valuable for measurements which require both exact position of the image and a constant and dependable time base (measurements such as burning rates of solids).

Camera speeds can be varied from 4 to 500 pps. In cameras like the Millikan, this is accomplished by changing motors; but in the newer cameras like Red Lake's LoCam, the speed is varied by continuously variable solid-state electronic control circuits.

## Rotating Prism Cameras

Because of their design, pin-type intermittent framing cameras are limited in speed to roughly 500 pps. To get higher framing rates a different type of camera must be used. The type most often used in combustion studies is the rotating prism camera. In contrast to the pin-type camera where the film advance is stopped for each exposure, in a high speed rotating prism camera the film runs continuously. In order to keep the image from being smeared on the film, the image must move, and film and image must be synchronized. This is accomplished via a rotating prism compensator. Light from the subject enters the camera through the camera lens, through the rotating prism, and then onto the film. Two types of the required mechanism are shown in Figures 2 and 3. The first figure shows the type of system used in the Fastax, Fairchild, Nova, Eastman, and Photo-Sonics rotating prism cameras. As shown, the prism and film advance sprockets are on separate shafts. Because it is difficult to exactly synchronize both shafts (primarily due to gear chatter and backlash), these types of cameras have problems with image smearing, especially at high speed. The system used by Red Lake's HYCAM is shown in Figure 3. In this system, the moving film, rather than gears, drives the prism shaft assembly. By eliminating gearing, the HYCAM takes the steadiest, highest resolution pictures of any rotating prism camera we have used--pictures comparable to those from the pin-drive cameras. Resolution to 68 line pairs/mm is claimed by the manufacturers at all speeds. Speed in the HYCAM is controlled electronically to within 1% up to 5000 pps. Maximum speed in the full frame format is 11,000 pps with 22,000 and 44,000 pps available in half-, and quarter-frame formats, respectively.

Accessories for the HYCAM include timing light generators (causes the edge of the film to be marked in 10, 100, 1000, or 10,000 timing marks/s), electronic flash synchronizers, auxiliary lenses for cine-oscillography, an accessory for streak photography, and various prism assemblies.

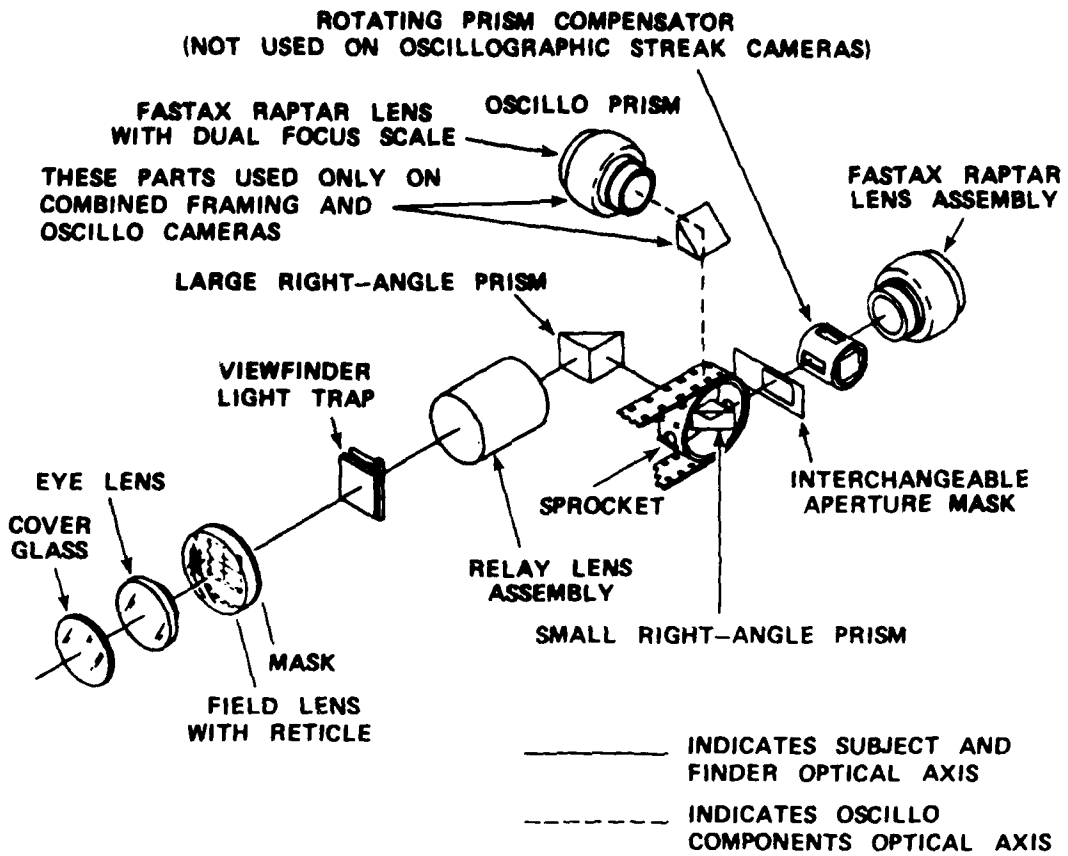



FIGURE 2. Fastax System. (Reproduced with permission of Red Lake Laboratories, Inc.)

## LENSES

There are several lens arrangements that could be used for cinephotomicrography of solid propellant combustion. Rather than discuss the various arrangements which could be used, the following discusses NWC's approach. The approach taken was to use a conventional thread-mount camera lens mounted on a lens extension tube. This arrangement is simple and provides a fairly rigid connection between the lens and camera body. Relative motion between the two is virtually absent.

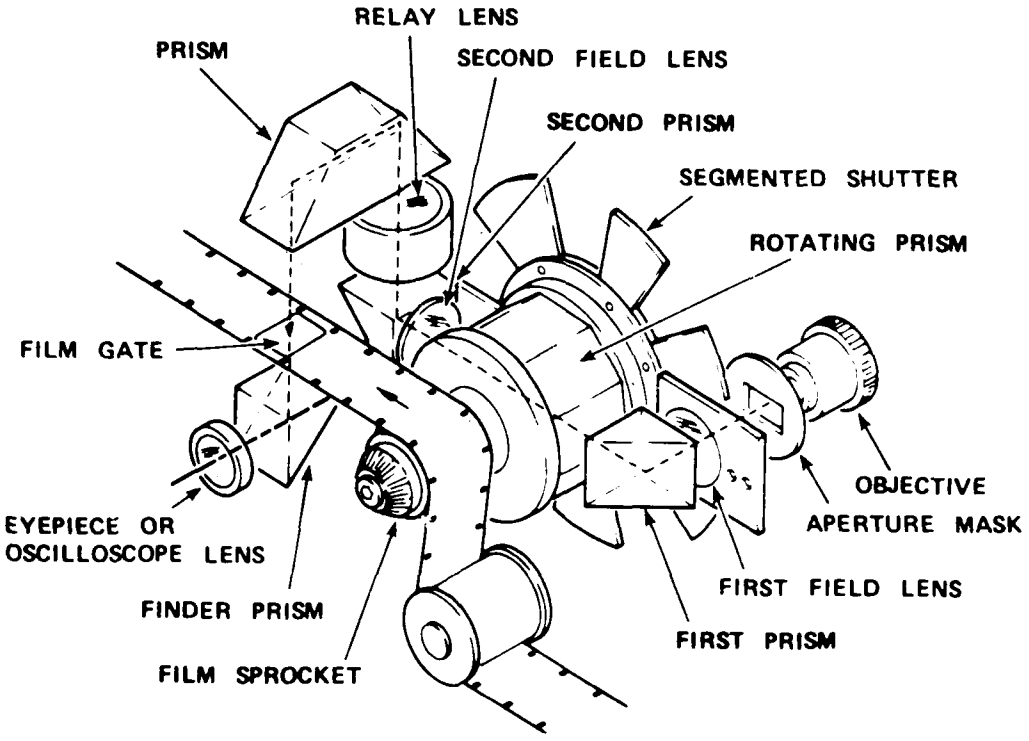



FIGURE 3. HYCAM System. (Reproduced with permission of Red Lake Laboratories, Inc.)

There are some considerations on the choice of the lens focal length. The most practical constraint is that the focal length has to be long enough for the lens to be located outside the combustion bomb with some additional clearance for focusing movement of the camera-lens system. Another consideration is that as one increases the focal length (with a given aperture opening) the resolving power of the lens decreases. Thus, if one chooses a focal length significantly longer than that needed to have the lens outside of the bomb, he will be sacrificing resolution.

A very important consideration as one goes to higher magnifications is the depth of field. Depth of field is determined, directly or indirectly, by lens focal length, f/stop, exposure time, and the intensity

of the external illumination. The influence of these factors will not be discussed here. An excellent treatment is found in a publication by Eastman-Kodak Company.[1] The depth of field and the resolution that was obtained under the constraints of NWC's cinephotographic system will be discussed later.

## WINDOW BOMBS

There is very little interest in the combustion of solid propellants at atmospheric pressure: most of the interest centers on propellants burning in a chamber at pressures comparable to those in rocket motor, i.e., several hundred psi. Obviously, if combustion of solid propellants at relevant pressures is to be studied, a pressure vessel must be used; one with windows for lighting and viewing if films of what is happening within the bomb are to be taken. There are basically five design considerations for a window bomb:

1. The bomb internal volume must be big enough to accommodate the sample and its smoke, and also big enough so that pressurization caused by burning of the sample is not too large. Loading density of less than 0.001 g of propellant per cubic centimeter of bomb volume is recommended. By limiting the loading density to less than 0.001 g/cm$^3$ the pressure rise due to the burning propellant should be less than 50 psi (344.7 kPa). Lower loading density will of course, give lower pressure rise.

2. The bomb must have walls strong enough to withstand the pressure.

3. Windows must be placed and sealed within these walls, and the windows must be capable of transmitting the light and holding pressure.

4. Access to the bomb must be provided for the sample and associated ignition equipment.

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[1]Eastman-Kodak Company. *Close-Up Photography and Photomacrography, Kodak Technical Publication N-12.* Rochester, N. Y., 1969.

5. Input taps through the walls or access plate (for ignition wires and thermocouple wires, for gas pressurization and purge, and for calorimeters) must be provided.

The above considerations for the design of a window bomb seem very simple and may be viewed in this way until it is realized (often through trial) that it is rather difficult to build a good one. The design of a window bomb is an exacting trade-off between lighting, pressure, sealing, materials, and application (how fast and at what magnification are you going to do your cinephotography) considerations. For example, design for low pressure (≈300 psi [≈2068 kPa]) combustion studies is relatively easy. The sample regresses slowly (≈0.1 cm/s) and therefore a slow framing speed is sufficient. Because the pressure is low, large windows can be used, and the bomb can be made from cheap and easily machined material with only a modest amount of attention to machining tolerances because sealing is not a difficult problem. Because the camera framing speed is low and the bomb windows large, lighting is not much of a problem. Thus, for these low pressures, the design of a window bomb is simple and good pictures can be expected.

As the desired pressure in the bomb is increased, everything begins to work against the designer. The sample burns faster, requiring a higher framing rate. All other things being equal, faster framing rates require more light on the sample. But larger windows cannot be used because of pressure effects--the higher the pressure the smaller (or stronger) the window needs to be. Also, as the pressure is increased, the bomb walls need to be thicker, so windows usually also get thicker. Trying to get a converging beam through a thick window may be difficult. As the pressure is increased, the seal problems become more critical and tolerancing needs to be improved.

The above is not a prelude to a text on window bomb design. It will not be discussed further in this paper except to point out that the design is not as simple as it might seem and to volunteer that NWC is willing to share the art of designing a good window bomb with anyone. NWC has two types of systems: the first is for pressures between 1 atmosphere and 1500 psi (10.34 MPa), and the second from 1000-10,000 psi (6.89-68.9 MPa). Many of the window bombs at other U.S. installations were made from prints of NWC's design.

The low pressure bomb (Figure 4) is constructed from 304 stainless steel to withstand the corrosive products from solid propellant ingredients. The body has an internal volume of about 450 ml with the

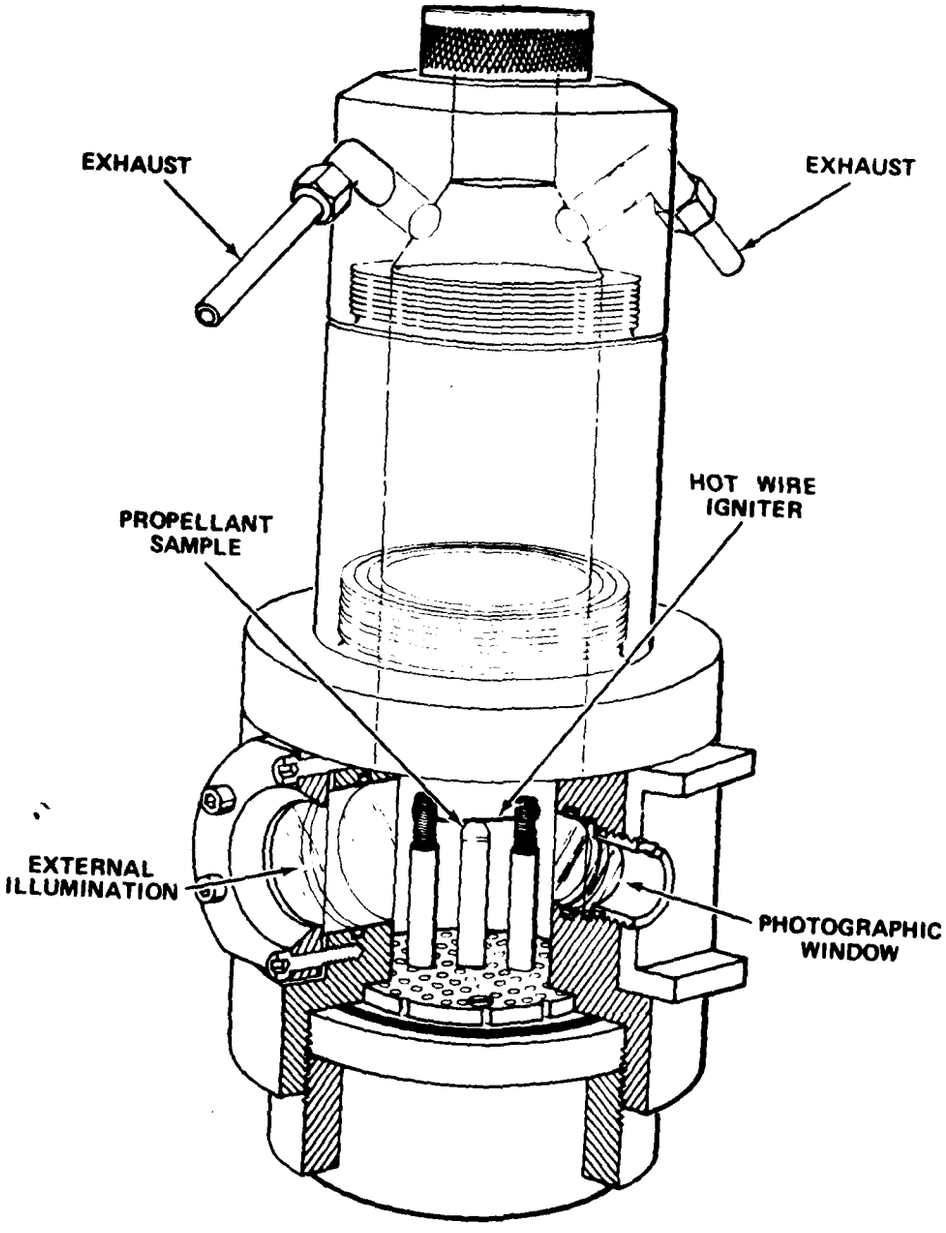



FIGURE 4. Low Pressure Combustion Bomb.

capability of increasing the volume by the addition of extension tubes to the upper part of the chamber. The interior of the bomb is 2 inches (5.08 cm) in diameter with 1-inch (2.54-cm) thick walls. The bomb has been pressure tested for a working pressure of 2,500 psi (17.24 MPa). There are three openings on the periphery of the bomb. One opening contains a sample viewing window made of General Electric 101 fused quartz measuring 0.750 inch (1.905 cm) diameter by 0.500-inch (1.27-cm) thick. Sixty degrees to this window is another window also made of GE 101 fused quartz measuring 1.500-inch (3.81-cm) diameter by 0.800-inch (2.04-cm) thick. This window is for external illumination of the sample. One hundred eighty degrees opposite the sample viewing (photographic) window is a 1.500-inch (3.81-cm) diameter opening in which a variety of plugs may be inserted for specific tests. This opening has been used for pressure or radiation transducers, or back lighting of the test samples. The top of the chamber may be fitted with a special adapter for rapid depressurization testing (as per Varney).[2] In addition, the bomb may be wrapped with heating elements for temperature sensitivity testing.

The sample holder (Figure 5) consists of a test base (A) which has an inlet port (B) for pressurizing gases and a flushing flow for the system, and two tapped holes for insulated electrical feed-throughs (C). A 10-μm (pore size) sintered stainless steel plate (D) placed above the gas inlet port diffuses the gas flow, giving a smooth flow pattern past the test sample. The terminal plate (E) attached to the top of the test base is made of 16-gage perforated stainless steel. The plate provides a mounting surface for the sample holder (F) and ignition posts (G) and also allows the proper air flow past the sample. The ignition system consists of two insulated electrical feed throughs (C) mounted in the test base. These insulated leads pass through the porous plate and are connected to the ignition posts mounted on the terminal base. The ignition posts are simply brass screws insulated from terminal base with micarta posts. The sample holder is attached to the terminal plate with a screw which allows an easy interchangeability of holders for different tests. The test base assembly is held in place in the combustion bomb (H) by means of a threaded ring (I). Proper orientation of the test base assembly is accomplished with a fixed pin (J) in the combustion bomb aligning with a hole in the test base assembly. The system is sealed with an O-ring (K) in the test base assembly.

[2] A. M. Varney. "An Experimental Investigation of the Burning Mechanisms of Ammonium Perchlorate Composite Solid Propellants," Ph.D. Thesis. Atlanta, Ga., Georgia Institute of Technology, May 1970. 226 pp.

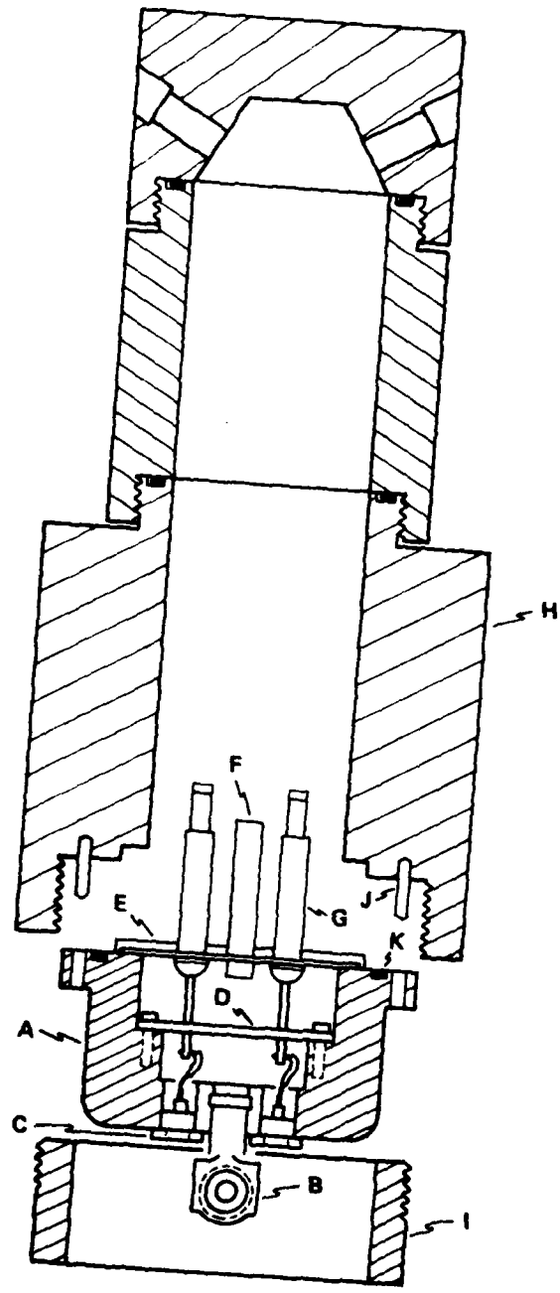



FIGURE 5. Sample Holder.

The high pressure bomb is essentially the same as the low pressure bomb except for thicker walls (2-3/8 inch [6.03 cm]), different window design, different electrical feed-throughs, and different closure (many heavy, square threads). The most serious problems are getting windows which will take the pressure and still pass enough light, and sealing the bomb at high pressures.

## LIGHT SOURCES

High light fluxes are required for high speed filming, especially at the higher framing rates with the associated extremely short exposure times. The studio-type floodlights commonly used in high speed photographic applications are impractical in combustion photography at high pressures. As mentioned earlier, from a lighting standpoint the quartz windows used in the pressurized window bomb should be as large as possible, but pressure considerations dictate that the window be as small as possible. This trade-off coupled with the requirement that the flux on the sample be high, makes the conventional methods of lighting for cinephotography impractical. A further requirement for photographing solid propellant combustion at high pressure is that the high light flux source should not cause excessive heating of the sample. For this reason, infrared filters are often used to prevent this part of the radiation from reaching the sample. In addition, the sample should be exposed to the light source only during the desired combustion event. Thus, some sort of shutter and timer is required.

The type of film to be used in the camera also partially determines the type of lighting to be used. In NWC's work, daylight color type film is preferred because of its higher speed and better color balance. Thus, the light source must match the daylight spectrum as closely as possible. Normally a 2500-W Xenon source in a Strong X-16 housing (one large single elliptical mirror with a small auxiliary elliptical reflector) is used, as shown in Figure 6.

At high pressure ($2{,}000 < p < 10{,}000$ psi), the above system is only marginally effective. For the high pressure work a more efficient Christie unit and a 1600-W Xenon bulb (bulbs up to 4200 W are available) are being used.

Another source of lighting is provided by the sample itself. Self-illumination is useful for studying the flames (if luminous) of burning solid propellant, as well as the combustion of metals. Although much

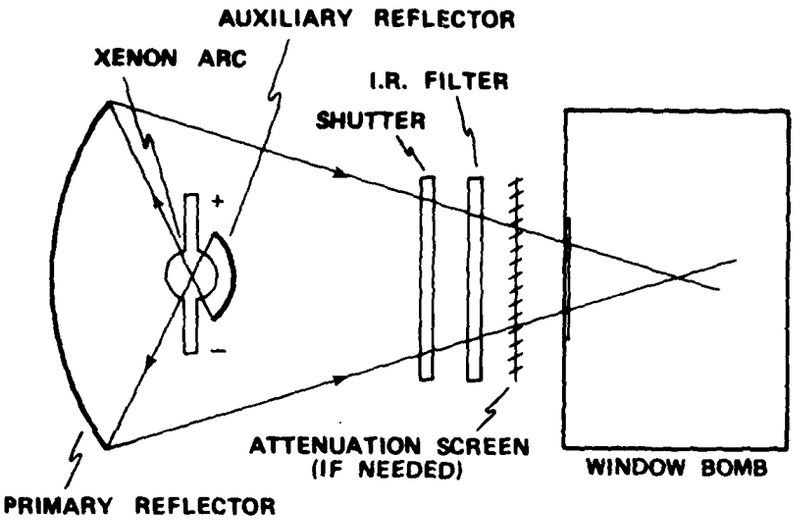



FIGURE 6. Schematic Representation of Xenon Arc, Ellipsoidal Mirror System Arc Image Furnace Showing Relative Locations of Major Components.

data can be obtained using self-illumination, a combination of self-illumination and alternate external illumination is usually even more effective. This combination of self- and external illumination is produced by chopping the external illumination. The resulting film alternates between several consecutive frames of self-illumination (showing such things as diffusion flames, metal combustion) and several frames of external illumination showing the activity occurring on the burning surface. This type of film is particularly useful in the study of metallized solid propellants. During the external illumination portion, for example, the viewer can see the surface regressing, metal particles accumulating on the surface, the coalescence of these particles into large agglomerates, and the residence of these large agglomerates on the surface. The self-illumination portion of the film clearly shows the ignition of aluminum particles, diffusion flames which often cause the ignition, and the subsequent combustion of the aluminum.

As mentioned earlier, an infrared filter is normally placed between the window bomb and the light source. Even with this protection, black colored samples often absorb enough energy to cause them to burn from

the side rather than from the top. In these cases, the beam is attenuated by decreasing the current to the Xenon lamp or by inserting wire mesh (window screen) attenuators between the light source and the bomb.

## NWC CINEPHOTOMICROGRAPHY SYSTEM

Specific components described above were combined to form the NWC low pressure system shown in Figure 7a. The components are the camera (HYCAM Model K2004E-115 or LOCAM), an 85 mm lens, various lens extension tubes, a low pressure (15-1500 psi [103-10,342 kPa]) window combustion bomb, an infrared filter (Dow Corning 4602) and a 2500-W Xenon light source (Strong X-16). The geometrical arrangement of the components is shown in Figure 7b. The high pressure system is essentially the same with the exception of the bomb and the Christie light source. NWC has extensive experience with the low pressure system and can offer a few practical suggestions for obtaining useful high speed films. People desiring information on setting up a high pressure system should contact the authors.

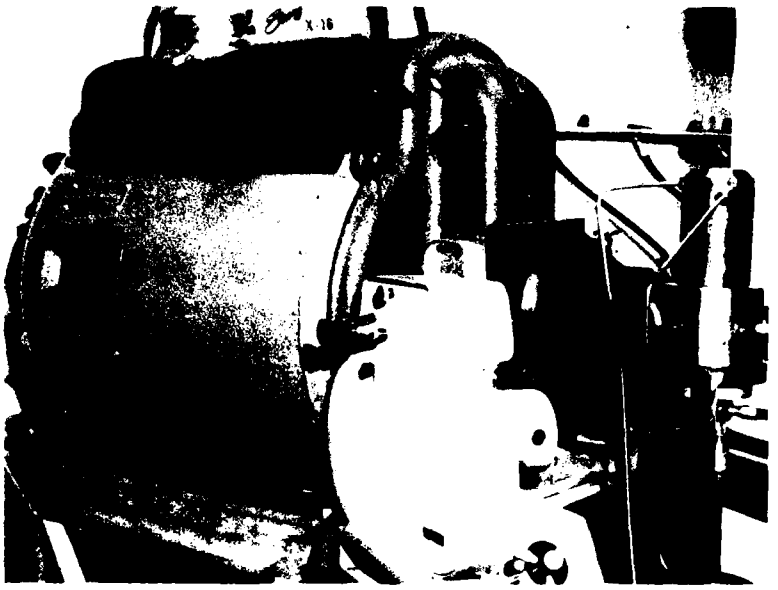
### Extension Tubes and Magnifications

The lens used at NWC is an 85 mm/f1.9 Pentax Super-Takumar lens. Three extension tubes which give nominal magnifications of 1X, 2X, and 4X are used. The extension tube lengths, the actual magnifications (subject/film image size), and the corresponding screen width of the projected film image are given in Table 2 for both the HYCAM and LOCAM cameras. (The difference in magnification between the cameras is due to the internal optics of the HYCAM.)

### Depth of Field

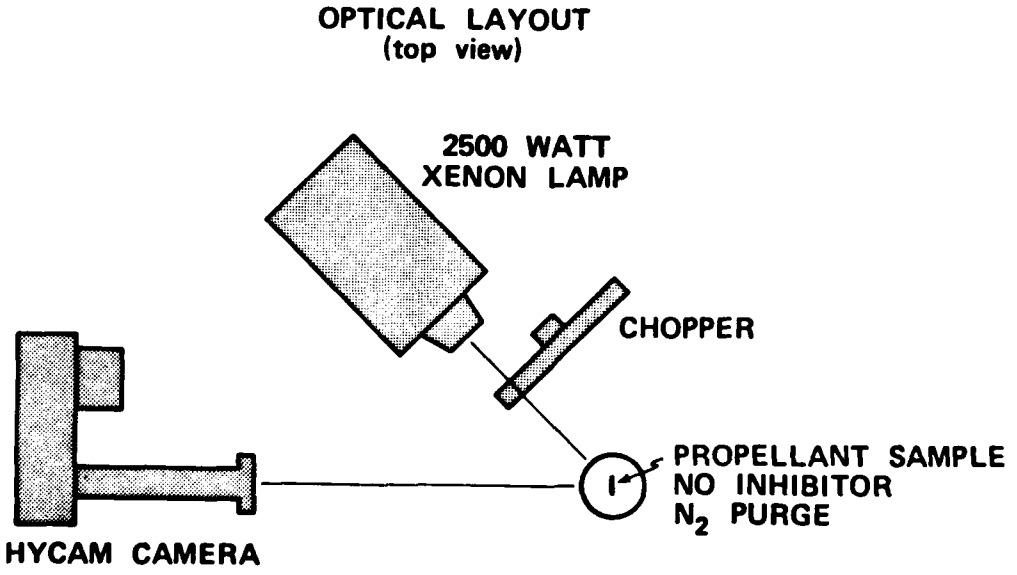
As the magnification is increased, the depth of field becomes an important consideration for combustion studies. At magnification of 2X and below, there have been no difficulties associated with depth of field. However, at 4X, the small depth of field is often troublesome. The approach has been, in general, to use the maximum external illumination consistent with minimal effect on the propellant combustion so that the lens could be stopped down giving a maximum depth of field.

As a guide, the depth of field for the 4X arrangement was determined. The information, depth of field versus f/stop, is given in Figure 8 for a 75 mm lens.



(a)

(1) High Speed Camera, (2) Photographic Bomb
(3) Xenon Source for Backlighting.




(b)
Geometrical Arrangement of System Components

FIGURE 7. Low Pressure NWC Cinephotomicrography System.

TABLE 2. Extension Tubes Used With the 85 mm/f1.9 Pentax Super-Takumar Lens.

| Magnification | Tube length, in. (cm) | Actual magnification | | Projected image,* μm | |
|---|---|---|---|---|---|
| | | HYCAM | LOCAM | HYCAM | LOCAM |
| 1X | 3.0 (7.62) | 1.08 | 0.89 | 9,713 | 11,786 |
| 2X | 6.16 (15.65) | 2.22 | 1.84 | 4,725 | 5,700 |
| 4X | 12.515 (31.788) | 4.56 | 3.77 | 2,300 | 2,782 |

*When projected, the full frame width corresponds to the given number of microns.

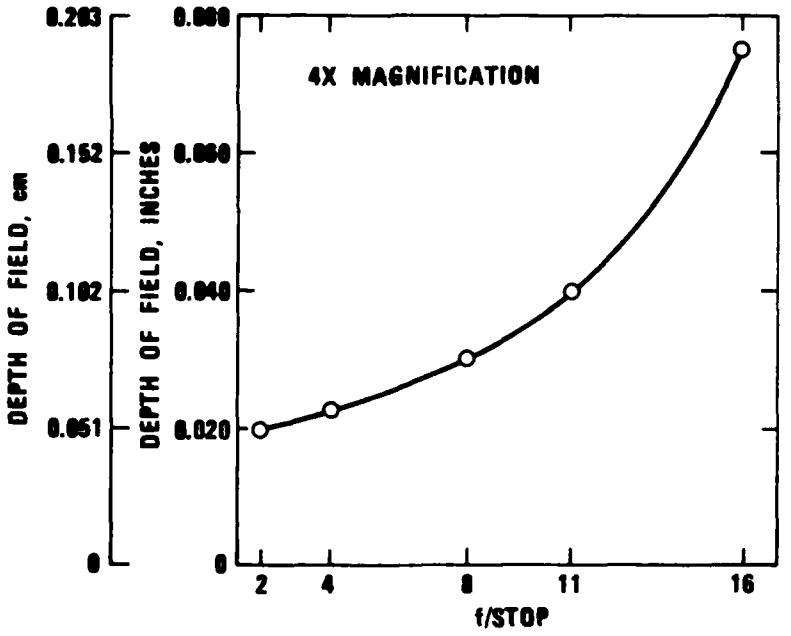



FIGURE 8. Depth of Field and f/stop at 4X Magnification for 75 mm Lens.

Most of the photography of aluminized propellants is done at 4X with a lens opening of f/11. This arrangement gives us a resolution of approximately 15 μm.

## Focusing

Proper focusing on the sample is of prime importance to ensure sharp pictures. Direct through-the-lens framing and focusing is provided on the cameras, making it possible to focus directly on the film.

In setting up for a test it is essential to focus the eyepiece on the crosshairs of the focusing screen to suit the individual eye. The lens should be set at the desired f/stop and the distance on infinity. Rough focusing is done by moving the entire camera, fine focusing by moving the index table the camera is mounted on. Once the front face of the sample has been brought into sharp focus, the camera is moved another 0.010-inch (0.254 cm) towards the sample. By doing this, the sharp focal point is moved inside the sample where the desired viewing area is located.

## External Illumination

The external illumination light source is an Osram 2500-W Xenon bulb mounted in a Strong X16 movie projection housing (Type 7600-2). The arc power is supplied by two direct current arc welder power supplies wired in series. The light source is placed 30 degrees to the optical path of the camera. An infrared filter is placed between light source and the sample to reduce the heat on the sample.

The arc source is operated at a constant power of 72 amps, while the proper flux level is obtained through adjustment of the main and auxillary reflectors. A flux level of 3.0 $cal/cm^2/s$ ($12.552 \times 10^4$ $W/m^2$) was determined to be the highest attainable level without prematurely igniting the sample. During setup, the calorimeter is inserted through the opening opposite of the photographic window so as to occupy the same spatial position in the bomb as the test sample.

## Some Exposure Guides

With ASA 125 film and external lighting from the 2500-W Xenon source, we use the following camera settings:

1. HYCAM - 4X, 4000 pps, f/11 camera aperture.
2. LOCAM - 1X, 400 pps, f/11 camera aperture.

## TIMERS AND SEQUENCERS

Proper sequencing of the system is accomplished using a six-channel sequencer. The channels control the start time of the camera, ignition, shutter for the Xenon light source, oscillograph, and the stopping of the camera. We typically use the following sequence: time = 0 camera start, oscillograph start; time = 0.3 s ignition, Xenon shutter open; and time = 5 s all stop. When partial burn samples for SEM are desired, another channel controls the time after ignition that a diaphragm is burst to depressurize the bomb and stop combustion before burnout of the sample.

The camera and other recording devices are normally started prior to ignition to insure their operating speeds have been reached (important in burn rate studies). The shutter on the light source remains closed until ignition to prevent unnecessary heating of the sample.

## HOT-STAGE MICROSCOPY

We have coupled the pin-type camera to an optical microscope to perform cinemicrography. The microscope is equipped with a hot stage (Figure 9) which can be heated at rates up to 85°C/minute. This combination of equipment was used extensively to study phase transitions and the decomposition of propellant oxidizers such as AP and HMX and the melting and agglomeration behavior of as-received and modified aluminum powders. A particularly interesting movie film was obtained which shows details of the phase transition orthorhombic to cubic of AP single crystals. The course of decomposition of spherical AP particles was also recorded by hot-stage cinemicrography. Evaluation of these recordings in a time-lapse mode revealed that the decomposition was via sublimation at 90 kPa pressure and at temperatures between 320-377°C. An activation energy of 28 kcal/mole was measured for the sublimation.

## MOTION ANALYZERS

There are two basic types of motion analyzers. One is simply a projector with special features for studying time-motion phenomena. Typical features include instant stop/start, single frame projection (for an unlimited time without film burning), forward/backward movement of the film at any point, frame counting, film reading, and various projection speeds (1-2-4-6-8-12-16 and 24 frames/s). This is a key

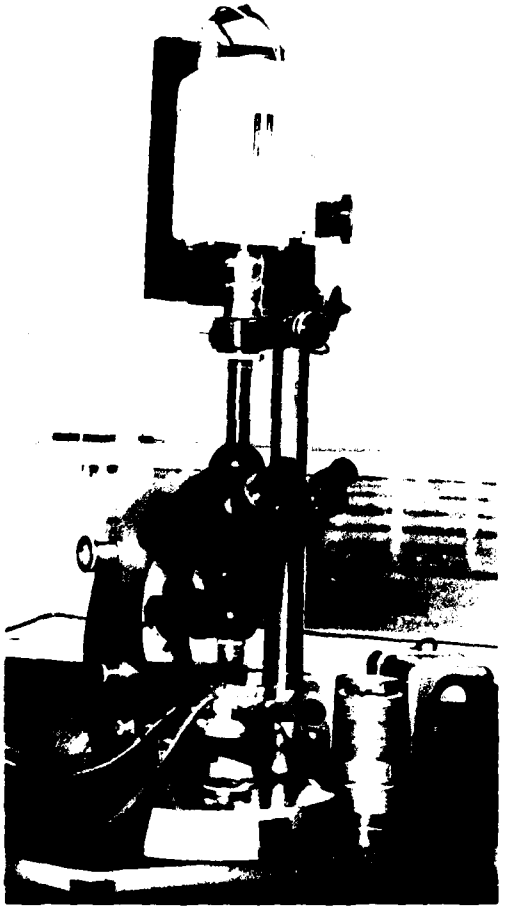


FIGURE 9. Hot Stage and Movie Camera Combined with Optical Microscope.

piece of equipment for any group seriously considering cinephotomicrography. NWC's analyzer has been used many thousands of hours, allowing viewing of many films in the cine mode and then viewing frame by frame. This was especially helpful in understanding the mechanisms by which small aluminum particles (1-40 μm) on the propellant surface agglomerate into big (≈ 100-500 μm diameter) particles of unburned aluminum.

The other type of motion analyzer employs precisely indexed movable hairlines in the X- and Y-directions, a framing head, and counter. The head advances the film and counts the number of frames (which, knowing the framing rate of the camera, gives a time), while the X- and Y-lines are used to measure the displacement of an item or surface, or the diameter of a particle (which, knowing the calibration, allows one to calculate distances). Knowing both distance and time, one can calculate rates. An analyzer of this type is used in the calculation of burn rates, and the accurate measurement of images on the film. For example, the cubic phase thickness and the regression rates of deflagrating single crystals of AP have been measured. Knowing the interrelationship between cubic phase thickness and burning rate, the phase transition temperature, and the thermo-physical properties of the AP, one can calculate the surface temperature (actually the temperature at the cubic-liquid phase interface) of the regressing AP. This measurement was not possible using other temperature measurement techniques.

## SUMMARY - CINEPHOTOMICROGRAPHY

Cinephotomicrography has been a very valuable tool for studying the combustion of solid propellants. If the old cliche "one picture is worth a thousand words" has any merit, then one reel of film must be worth a few million words.

A cinephotomicrography system can range from the very simple and inexpensive to very sophisticated and moderately expensive. In order to study combustion of solid propellants, one needs (each of these items was discussed in the text):

A high speed camera, either pin-type or rotating prism
A window bomb
A light source (film matched to light source)
A timer/sequencer
Infrared filters
A motion analyzer/projector

Other items which are useful include hot-stage microscope and adapters for cinephotography, light attenuators, several lenses and extensions, oscillo and streak accessories for the camera, and extension tubes for the camera.

## SCANNING ELECTRON MICROSCOPY

### BACKGROUND

Microscopy is the use of devices to form magnified images of small objects. The most familiar is the optical microscope which, by way of lens systems, forms images of objects illuminated with visible light. Instead of light beams focused by optical lenses, an electron microscope uses a beam of electrons focused through electromagnetic lenses. The scanning in SEM means that an electron beam is scanned over a sample in raster fashion. As a result of interaction of the beam with the sample, emission occurs and can be detected, collected, and amplified.

Although the SEM is a rather sophisticated piece of equipment, the use of the device is relatively simple. It is not the purpose of this paper to discuss the details of the SEM (references are included in the bibliography). A brief description of the principles and components making up an SEM is given below, to facilitate the understanding of how a beam of electrons scanned over the sample can image the topology (and indicate some surface chemical composition) of a sample.

#### Principle

The principle of the SEM is illustrated in Figure 10. A finely focused electron beam impinges on a point on the sample surface. This electron beam interacts with the sample causing several types of emissions (discussed more fully later). These emissions are then collected and amplified. The amplified signal then controls the brightness on a cathode ray tube. To get an image of an area on the sample, one simply needs a composite of these point-originated signals. To obtain signals from an area, the electron beam is scanned over the sample in a raster fashion. The scan of the cathode ray tube is scanned synchronously with the electron beam. Thus the cathode ray tube collects and displays a series of these point signals as areas of relative brightness. Changes in brightness represent changes in property (topology, chemical composition, electronic conduction, etc.) of the scanned surface.

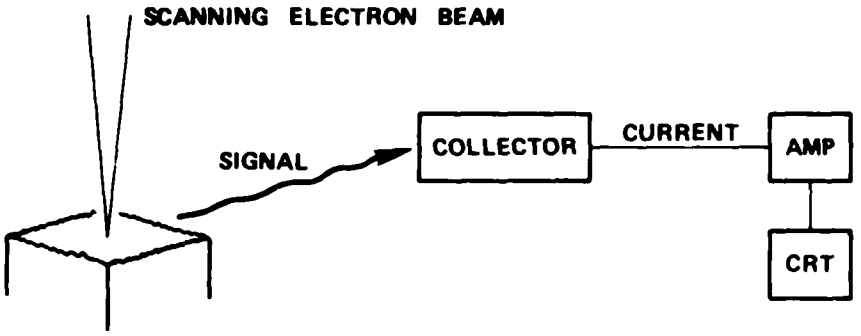



FIGURE 10. The Principle of the SEM.

Interaction of the Electron Beam With the Sample

The basic principle for the SEM is the same as that used in the X-ray microanalyzer and other microprobe type instruments used to detect chemical composition of the sample. In all these instruments the specimen is irradiated by a finely focused beam of electrons, and several types of emissions are released from the sample as illustrated in Figure 11.

The secondary electron signal is particularly useful for determining the topology of a sample because its level is particularly dependent on topography. The signal varies as the slope of the sample changes. The reason for this is outside the scope of this article but interested readers may find a detailed explanation on pages 24-39 of Hearle, Sparrow, and Cross.[3] Suffice it to say that an image produced on the cathode ray tube by the collection and amplification of secondary electrons generated as the electron beam scans the specimen is readily interpreted by the human eye in terms of surface topography.

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[3]J. W. S. Hearle, J. T. Sparrow, and P. M. Cross. *The Use of the Scanning Electron Microscope*, Pergammon Press, 1972.

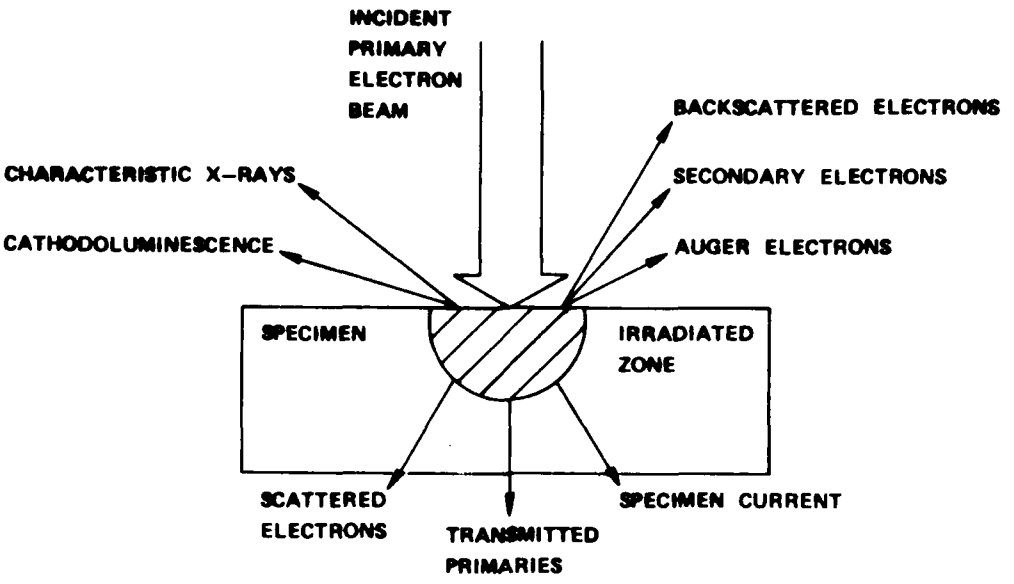


FIGURE 11. Commonly Used Contrast Mechanisms.

The X-rays are the other signals of interest for combustion diagnostics. If, when the electron beam strikes the sample, an inner shell electron is excited to leave an atom or go into a higher unoccupied level, and this electron is replaced by one of the outer shell electrons, an X-ray photon is emitted. The energy of this X-ray photon is the same as the difference between the energy levels in the atom, and these values are different and unique for the different elements. Later sections will discuss how these signals are analyzed.

The other types of emission caused by the incident electron beam are presently not of interest for combustion diagnostics. A detailed discussion can be found in several sections of Ref. 3.

Components of an SEM

The essential components of an SEM are: an electron source, a means of focusing a small beam of electrons from the source onto the specimen, a means of scanning the spot across the sample, a means of collecting signal(s) from the sample, a means of transmitting and amplifying the signal(s), and a display system capable of being scanned synchronously with the incident scan. This set of components and their relationship is shown in Figure 12.

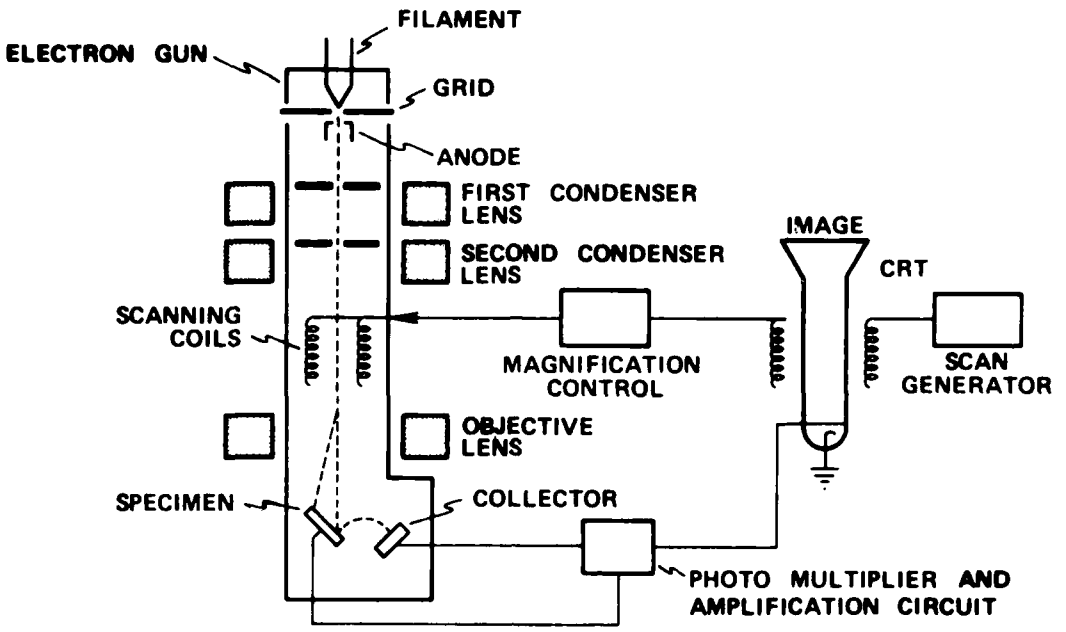


FIGURE 12. Diagrammatic Illustration of the SEM. (From "Metallurgical Microscope," by F. F. Asbury and C. Baker. Copyright © "Metals and Materials," The Metals Society, London.)

The electron source is usually a hot tungsten cathode. There are two new types of electron guns which can give greater beam current than the hot tungsten source. The first is the heated lanthanum hexaboride emitter which can give currents 5-10 times greater than the tungsten. The second is the field emission gun with beam currents 50-100 times larger. These latter two sources are mentioned here because their higher beam current is useful in X-ray detection. The electrons are accelerated towards the anode which is at ground compared to the 1.0-3.0 kV at the cathode. The accelerated electrons then pass through one or more electron lenses to focus the beam to a diameter of a few nanometers. A scan generator coil deflects the electron path moving the few-nanometer-diameter beam over the sample surface. As discussed earlier, the beam and sample interact. For topology, the secondary electrons are collected as shown in Figure 13. There is no need to focus the secondary electrons because at any given instant all the secondary electrons are coming from the same spot on the sample.

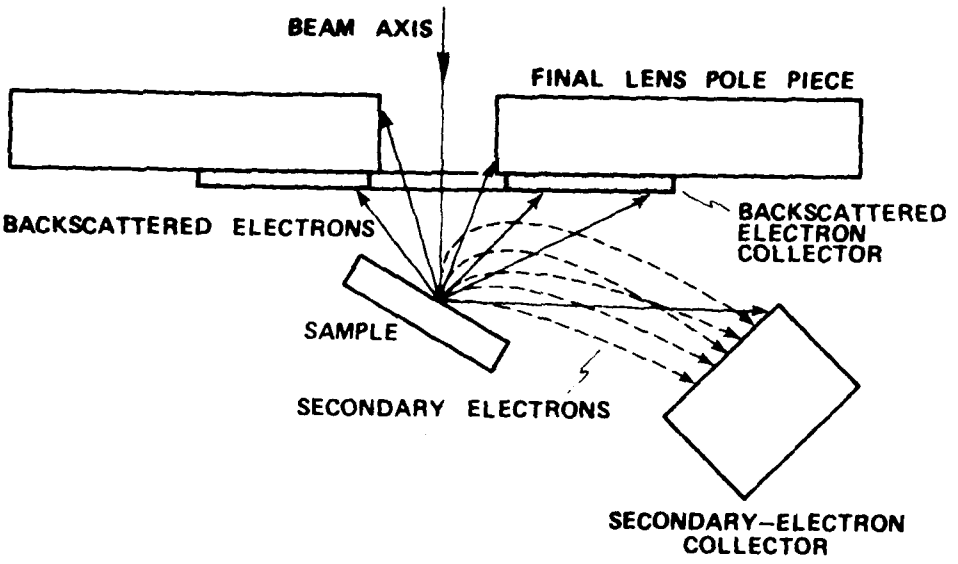


FIGURE 13. Collection of Secondary Electrons. (From "The Scanning Electron Microscope," by Thomas E. Everhart and Thomas L. Haves. Copyright © January 1972, Scientific American, Inc. All rights reserved.)

Once the secondary electrons have been converted to photons via the scintillator, they are transmitted via a light pipe to photomultipliers where photoelectrons are excited (Figure 14). Each photoelectron triggers a cascade yielding from $10^5$ to $10^7$ additional electrons. This current is further amplified electronically and then the signal is sent to a cathode ray tube scanned synchronously with the original incident beam.

This, briefly, is the SEM. Further detail and design is beyond the scope of this paper and not necessary for operation of any of the commercially available SEMs. In fact, the level of detail presented above may not even be necessary because many of the new machines are virtually impossible to damage because of operator error. The operator only has to load his specimen into the chamber, flip the right switches and take pictures.

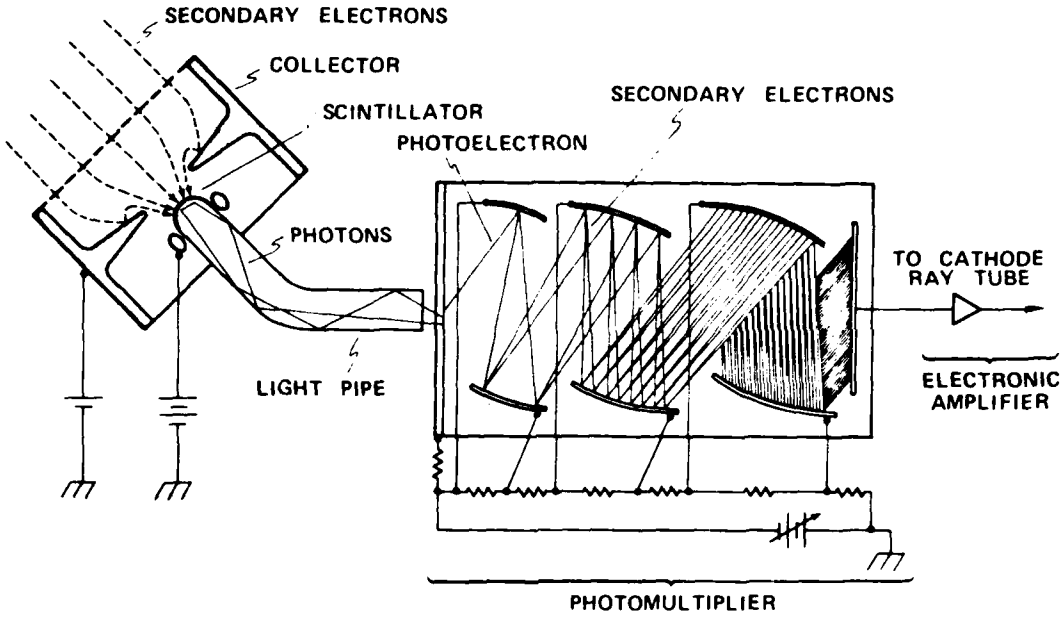


FIGURE 14. Amplification of Signal. (From "Scanning Electron Microscope," by Thomas E. Everhart and Thomas L. Hayes. Copyright © January 1972, Scientific American, Inc. All rights reserved.)

## Advantages of the SEM

We are all familiar with the optical microscope. Many of the problems of optical microscopy have been overcome in scanning electron microscopy. One of the chief limitations associated with optical microscopy, especially at high magnifications, is depth of focus. At 10X much of the image of a rough sample will be out of focus at any given focus. The SEM with its several hundred fold increase in depth of focus (see Figure 15), may show the same sample in focus throughout. Except for color, the SEM usually provides much better contrast than does the optical microscope. The resolution advantage of the SEM over the optical microscope is shown below.

| | Optical | SEM |
|---|---|---|
| Resolution | 0.2-5 μm | 100 Å-0.2 μm |

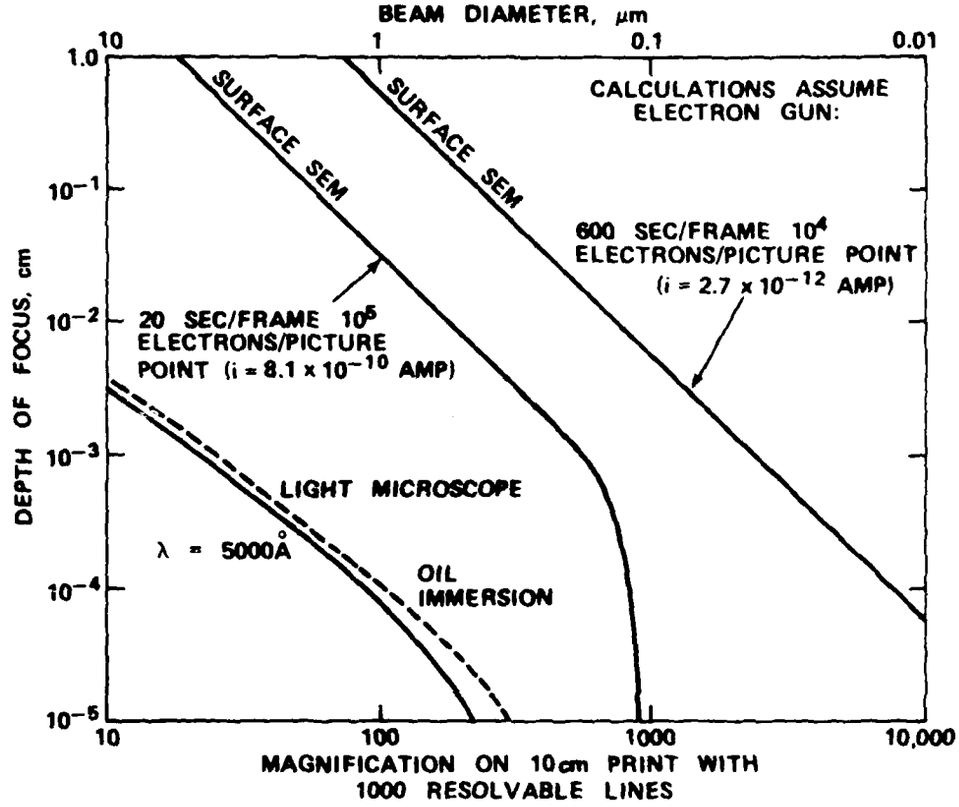


FIGURE 15. Depth of Focus of Optical Microscope and Surface SEM. (Copyright © A. D. G. Steward, Cambridge Instruments, London.)

In magnifying power the SEM has a range from 15 to 100,000X compared to the limited range of the optical device. In addition the SEM can zoom up and down in magnification without changing the focus while the optical microscope must be focused with each change of lens. The optical microscope provides only an image while the SEM provides an electrical signal which may be processed.

Apart from its cost, the disadvantages of an SEM are: (1) the samples often need to be coated, (2) the samples must be placed in a vacuum environment, (3) sample color contrast is lost, (4) translucent

samples are not viewed in transmitted illumination (also polarizers are not used), and (5) identification of surface compounds is not easy.

## SEM AND SOLID PROPELLANT COMBUSTION SAMPLES

A piece of solid propellant which is burning cannot be viewed using an SEM. In order to view the surface of the sample we must first quench the combustion.

### Quench System

There are essentially two methods of quenching burning materials. One can either remove one or more constituents essential for combustion or one can cool the sample. Most quench techniques have some aspects of both methods.

The most popular techniques are: (1) rapid depressurization of the combustion chamber, (2) thermal quench using a cold plate or vise, and (3) immersion in a coolant. For samples whose burning is governed by gas phase reactions and which is burning at elevated pressure, the rapid depressurization method is best. In these tests, the combustion chamber is equipped with a burst diaphragm. At some time during the test this diaphragm is ruptured. The gas phase reactants are removed from near the surface, the chamber gases are cooled by the rapid expansion, and the sample is quenched. Studies have shown that the rate of depressurization is critical in the quench process.[4] If the dp/dt is too low, the sample may continue to react after the diaphragm has burst before being extinguished. If this were to occur, some artifacts could appear on the sample. Steinz and Selzer have shown[4] that for composite solid propellants, depressurization rates of approximately $10^4$ psi/s (689.48 MPa/s) are required to permanently extinguish propellants. This verifies the values of $5 \times 10^4$ psi/s ($34.47 \times 10^2$ MPa/s) at 400 psi (2.76 MPa) to $2.5 \times 10^5$ psi/s ($17.24 \times 10^2$ MPa/s) at 1500 psi (10.34 MPa), determined much earlier by Ciepluch.[5]

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[4] J. A. Steinz and H. Selzer. "Depressurization Extinguishment of Composite Solid Propellants: Flame Structure, Surface Characteristics and Restart Capability," *COMBUST SCI TECHNOL*, Vol. 3 (1971), pp. 25-36.

[5] C. C. Ciepluch. "Effect of Rapid Pressure Decay on Solid Propellant Combustion," *AMER ROCKET SOC, J*, Vol. 31 (1961), pp. 1584-1586.

At NWC we use a modification to our window bomb that was developed by Varney.[2] Varney used layers of mylar as the diaphragm material. Our slight modification of Varney's method is shown in Figure 16. The diameter of the opening is 1.5 inches (3.81 cm) and the assembly serves as the upper cap to our bomb. The mylar discs are 0.005-inch (0.0127 cm) thick and the number to be used depends on the bomb pressure as given in Table 3.

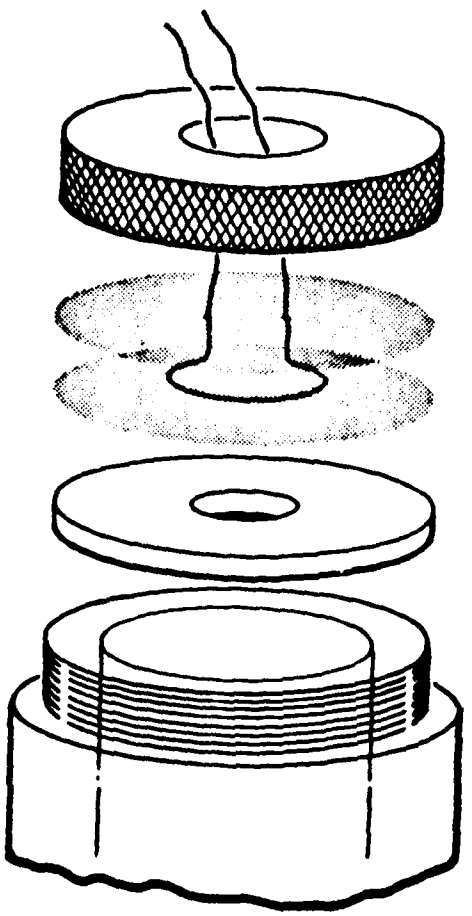

FIGURE 16. Rapid Depressurization Quench Apparatus.
(The authors are indebted to A. M. Varney for this device.)

TABLE 3. Mylar Discs as Burst Diaphragm for Depressurization of NWC Combustion Bomb

| Bomb pressure, psia (MPa) | Number of discs |
|---|---|
| 100 (0.689) | 1 |
| 200 (1.379) | 2 |
| 300 (2.068) | 3 |
| 400 (2.758) | 3 |
| 500 (3.447) | 4 |
| 600 (4.137) | 5 |
| 700 (4.826) | 5 |
| 800 (5.516) | 6 |
| 900 (6.205) | 7 |
| 1,000 (6.895) | 8 |
| 1,100 (7.584) | 8 |
| 1,200 (8.274) | 9 |
| 1,300 (8.963) | 9 |
| 1,400 (9.653) | 10 |
| 1,500 (10.342) | 11 |
| 1,600 (11.032) | 11 |
| 1,700 (11.721) | 12 |
| 1,800 (12.411) | 13 |

The wire used to cut the top mylar disc (not included in the number given in Table 3) is 0.010-inch (0.0254 cm) Nichrome sandwiched between the stack of discs and the top disc, and heated by 110 VAC. This method of venting gave dp/dt values greater than the $10^6$ psi/s ($68.95 \times 10^3$ MPa/s) we were able to obtain using a mechanical vent release device.[6]

It is not always possible to use a rapid depressurization quench. Some of the situations where this type of quench is not desirable are: when the pressure in the bomb is low, when the surface structure of the sample is very frangible, when the pressure of the bomb is very high (extremely high dp/dt not only quenches samples, it can destroy equipment), and when the combustion of the sample is governed by condensed

[6]J. D. Hightower and E. W. Price. "Experimental Studies Relating to the Combustion Mechanism of Composite Propellants," *ASTRONAUTICA ACTA*, Vol. 14, No. 1 (1968), pp. 11-21.

phase reactions. One way of overcoming some of the above obstacles is by using a thermal quench. This is particularly useful when either thin samples, or samples which are condensed phase reaction controlled, are to be quenched. We have used a copper vise (which could be cooled by liquid nitrogen) to thermally quench samples at low pressures, and also when thin samples of AP crystals were burned.[7] Similarly, single particles of metal are quenched from burning at 1 atmosphere by impacting on metal plates.[8] Others have tried to thermally quench samples by immersing them into a coolant such as liquid nitrogen or alcohol. Our experience has shown that this is not a good approach since the liquid quickly vaporizes and a boiling ensues: portions of the sample may be damaged by the agitation and some of the sample may be separated from the cold liquid by an insulation of the gas. The investigator probably would be more successful using a liquid nitrogen-cooled copper vise.

Whatever the quench technique, it must be remembered that no quenching process is without artifacts. Whatever the method of quenching burning samples, it must be assumed that some relevant details will disappear and some quench-dependent effects may be introduced during quenching (or possibly during storage, coating, and inspection). In our studies, combustion behavior is not inferred solely based on micrographs; several experimental techniques which are complementary in nature, have been used. The most decisive type of data that can be used in such correlations is that involving real time observations. Thus, by using cinephotomicrography we have observed features not only during combustion but we have observed the changes of these features during quenching, even to the point of subsequently locating specific surface features (seen in the motion pictures) on the quenched sample. *Combustion studies which present conclusions based solely on SEM, without the benefit of agreement with different observations (especially real time observations) should be accepted only with reservation.*

## The Coating

Most samples, especially propellant samples, are coated before examination in the SEM. This coating is a few hundred angstroms of carbon or some heavy metal (usually gold-palladium that is so thin

[7]Naval Weapons Center. *Decomposition and Deflagration of Ammonium Perchlorate*, by T. L. Boggs and K. J. Kraeutle. China Lake, Calif., NWC, October 1968. 54 pp. (NWC TP 4630, publication UNCLASSIFIED.)

[8]J. L. Prentice. "Combustion of Pulse-Heated Single Particles of Aluminum and Beryllium," *COMBUST SCI TECHNOL*, Vol. 3, No. 6 (August 1971), pp. 387-98.

it does not obscure surface details). The conductive coating does several things which improve the image. The metal layer keeps a sample from "charging" (which "whites" out the CRT and hence the photograph corresponding to that portion of the sample which is charging) by conducting the electrical charge from the surface to the grounded aluminum sample pedestal. The metals are also usually better emitters of secondary electrons than the underlying sample, and as such, provide a better image.

Since most laboratories which have SEM equipment also have coating equipment and operators to perform these tasks, we will not go into much more detail here. Additional detail may be found in Chapter 4 of Ref. 3.

The coating can lead to some artifacts. Sometimes subsequent to the coating, the thin metal layer may crack or "patches" pull free from the surface. When viewed with the SEM these areas will appear black because of the lower emission of secondary electrons from the uncoated area relative to the coated area. One has to be careful to not interpret these areas as being deep fissures.

Image From SEM

The image which is displayed on the CRT is often photographed using a Polaroid camera with positive or positive/negative film. Other cameras could, of course, be used but the "instant" positive available with Polaroid is almost a necessity since the brightness and resolution of the image on the CRT are functions of so many variables (sample tilt, sample composition, filament current, orientation of sample with respect to the collector, black level, photomultiplier voltage). An operator usually sets up the image as best as possible, takes a Polaroid picture, and, based on the resulting picture, makes adjustments until the desired result is obtained.

In attempting to make measurements from micrograph, the reader is cautioned to remember that the sample is at an angle to the primary beam and the collector, and what appears to be at right angle to the viewer may actually be skewed. Because of the great depth of focus and the variation of focus with working distance, care must be exercised on samples having significant surface relief. It is outside the scope of this report to discuss the problem of mensuration from SEM micrographs. An excellent discussion is contained in Chapter 11 of Ref. 3.

In the work done at NWC it was found to be extremely useful to put a length indicator bar on the micrographs. This was accomplished as shown in Figure 17. The positive Polaroid is mounted on heavy card stock which has registration holes punched in it. We have a series of "masks" corresponding to different magnifications. The proper mask is placed over the positive Polaroid, the ensemble is photographed, and a negative is made. This allows us to enlarge or reduce, in printing, the image size and yet the indicator is similarly changed in size. This is a significant advantage over the old method of only giving a magnification (e.g., 1000X) since the magnification may have changed as the image was enlarged or reduced in printing. When one publishes micrographs in several journals, each with slightly different format requirements, the savings in time during writing and publication more than makes up for the initial investment in time.

The purpose of putting a length indicator bar on the micrographs is not for precise measurement. It is simply there so that one can "get a feel" for the sizes of objects.

Stereo-pairs--two micrographs of the same area with a slight difference in the tilt angle of the specimen (usually less than 10 degrees)--give the appearance of three dimensions when viewed using a spectral stereo viewer. On complex samples this is a necessity because often optical illusions occur, a rounded depression appears to be protruding from the surface as opposed to its true configuration. In addition, measurements using aerial photoreconnaissance techniques can be made.

Other imaging devices include TV sets: instead of the image being displayed on a CRT it is displayed on TV. The higher sweep rates and larger screen size make it easier (and less tiring, especially for a whole day of viewing) to investigate samples having detailed topography. Another imaging device includes feeding the signal into a computer, rather than a CRT. Much of this work is in a developmental state at this time, but it appears that promising advances will be made.

Samples can be looked at without coating but only if the accelerating voltage is decreased to 1-5 kV or if one of the newer electron sources ($LaB_6$ or field emission) is used.

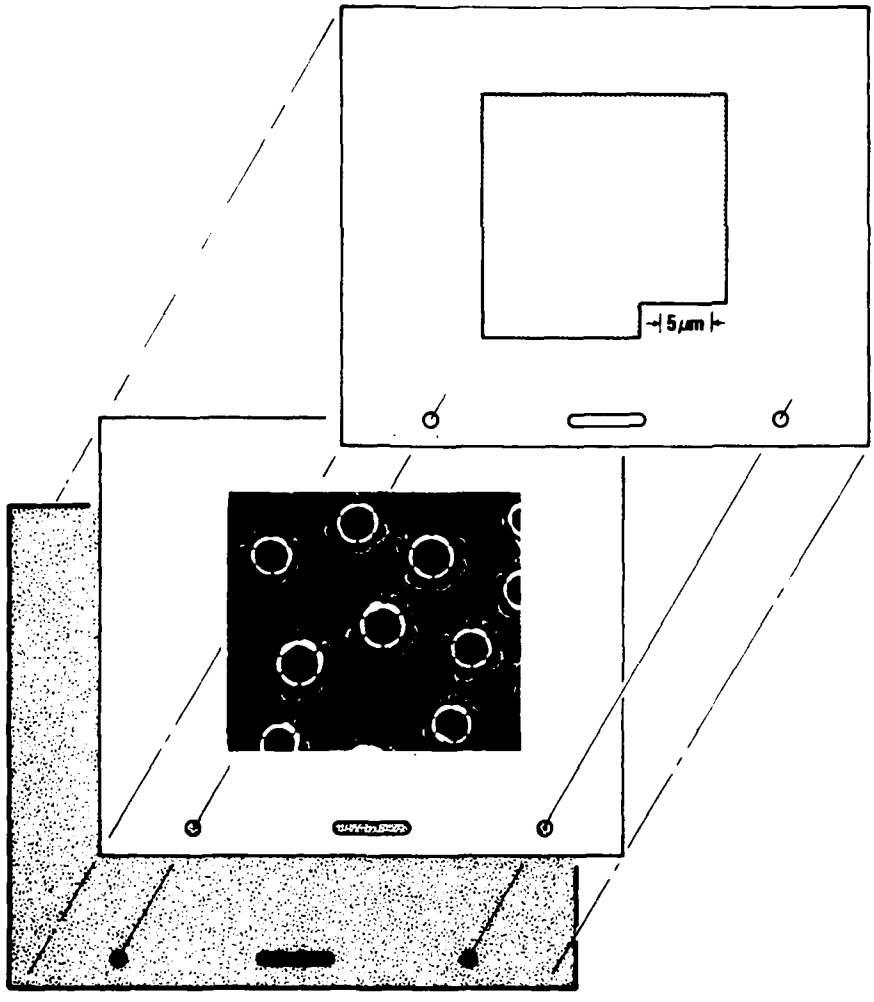


FIGURE 17. A Simple Method for Putting a Size Designation on Micrographs.

## MICROANALYZER OR SEMs WITH ADDED X-RAY ANALYZERS

In an earlier section it was mentioned that the incident electron beam could cause X-ray photons to be liberated from the irradiated sample, and that the energy of the liberated photon is different and unique for each of the different elements. In this regard an SEM is

remarkably similar to the electron probe microanalyzer, except that the SEM's requirements of image resolution (> 250 angstroms) necessitate the SEM using much lower beam intensities than the microprobe. For this reason the conventional type of X-ray spectrometers used in microprobes are impractical for use with the SEM.

The conventional electron probe uses X-ray spectrometers to measure, identify, and count the X-rays based on their wavelengths. Remembering that the energy of each X-ray photon is the transition between orbital shells in the atom and is unique for each atom, the equivalent wavelength from $\lambda = hc/E$ will be different and unique for each atom. Diffraction, described by Bragg's law ($n\lambda = 2d \sin\theta$), using crystals with known d spacing, can be used to separate the various wavelengths. Spectrometers of this type are called wavelength dispersive (WD). To cover the whole range, WD spectrometers are usually equipped with many crystals. Even then, considerable time is needed to obtain an overall spectrum of all elements present on the specimen surface. The resolution of the crystal in separating the X-ray wavelengths is good ($\sim$ 10 eV), but its efficiency is very poor. This collection efficiency can be improved using curved crystals and fully focusing diffractometers.

The WD spectrometers have problems other than requiring several crystals and considerable time to analyze a sample. Because of their construction, fully focusing WD spectrometers are not suitable for rough surfaces (such as quenched propellants).

Because of some of these problems, energy dispersive (ED) spectrometers are often used with SEMs. The ED X-ray attachments consist of a lithium drifted silicon crystal, a multi-channel analyzer, and necessary electronics. In these devices an incoming X-ray photon is converted into an electronic pulse in the lithium drifted silicon crystal. A bias voltage applied to the crystal collects this charge which is proportional to the energy of the X-ray. This pulse is amplified, converted to a voltage pulse, and fed into a multi-channel analyzer. The analyzer sorts out the pulses according to their energy and stores them in the memory of the correct channel. The resulting spectrum can be displayed on a CRT, plotted on a chart, or printed out numerically.

The resolution of the ED system is much poorer than that of the WD systems. In most applications this is not a severe limitation because most elements above sodium (atomic number 11) are readily detected. Unfortunately for the person concerned with propellant samples, ED cannot be used to separate F, O, N, C, or B -- all elements we might be

interested in. It can, on the other hand, distinguish Mg, Al, Cl, K, Cr, Fe, Cu, and Zr. The WD spectrometers, used with a microprobe analyzer, can get down to Be.

Thus the person interested in all elements present in propellants and on the surface of quenched propellant samples has a problem. One method (ED) is simple and fast, but cannot discriminate between F, O, N, C, or B -- it can be used for Mg, Al, Cl, K, Cr, Fe, Cu, and Zr. The other, slower and more cumbersome method, can detect all elements above Be. For analysis of an aluminized composite propellant having AP, HMX, and an organic binder, both WD and ED techniques must be used to provide a complete compositional mapping.

## EXAMPLES

In the preceding sections the devices have been discussed and, in some cases, examples of the use were cited. Because of space limitations, it is not feasible to further discuss the details of how the devices were used and the results. The following bibliography is presented for those who would like these details.

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